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DISSOLUTION RATES OF POLY(METHYL METHACRYLATE) IN MIXTURES OF
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by

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As predicted by thermodynamic studies of polymer conformation, high molecular weight poly(methyl methacrylate), PMMA, dissolves cleanly, and at a constant rate, in a 7:3 mixture of 1-butanol and acetonitrile although neither liquid is a solvent for PMMA by itself. Mixtures of other alcohols with acetonitrile also dissolve PMMA. When mixtures with the same fraction of acetonitrile are compared, methanol dissolves PMMA almost twice as fast, ethanol and hexanol at about the same rate, and 2-propanol somewhat more slowly than the 1-butanol mixture with acetonitrile. The measurements of dissolution rate were made using a laser interferometer at 20°C.

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Dissolution Rates of Poly(Methyl Methacrylate)

in Mixtures of Non-Solvents*

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The combination of two or more non-solvents to produce a solvent mixture for a polymer is of practical importance in many applications. The coatings industry is the most obvious example, although the definition of a "good" solvent may not always agree with a thermodynamic view. From the standpoint of the formulator of nitrocellulose lacquers, for example, a solvent with superior "solvent power" is one which gives the lowest viscosity for a given polymer at a fixed concentration[1]. On the other hand, the most compatible solvent from the thermodynamic standpont is one which gives the highest viscosity corresponding to the maximum expansion to the individual polymer chains. Nitrocellulose lacquers often are formulated with mixtures of solvents including diluents which are, themselves, not solvents for the polymer.

Interaction of a polymer with solvents can be quantified using various criteria. Intrinsic viscosity, [η], is a direct measure of chain expansion as indicated by the expression[2]:

$$[\eta] = \phi(\overline{r^2})^{3/2}/M \qquad (1)$$

where $(\overline{r^2})^{1/2}$ is the root-mean-square end-to-end distance for a chain of molecular weight M and ø is Flory's "Universal constant", with a value of 2.1 x10^{21} where [η] is in dL/g and r is in cm. The minimum value of intrinsic viscosity is attained in the poorest solvent. The value of $(r^2)^{1/2}$ is the "unperturbed" dimension which will be obtained in a theta (or Flory) solvent where polymer of infinite molecular weight precipitates. The same value of $(r^2)^{1/2}$ is expected in to be found in the melt state at the same temperature. As part of a general study of cosolvency, mixtures of n-butanol with acetonitrile were reported by Prolongo et al as solvents for poly(methyl methacrylate), PMMA[3]. Neither the alcohol nor the acetonitrile by itself dissolves high molecular weight PMMA at 25°C. Intrinsic viscosity was found to reach a maximum at about 0.55 volume fraction of acetonitrile (Figure 1). This was true for PMMA samples with maximum intrinsic viscosities ranging from 0.2 to 0.8 dL/g.

In further work, the same group[4] used light scattering to establish the second virial coefficient, A_2, for PMMA in mixtures of several alcohols with acetonitrile. The values of A_2 were taken from the slope of the usual plots of the concentration to light scattering ratio versus concentration. A value of zero for A_2 is expected in the theta condition. Both intrinsic viscosity and second virial coefficient (Figure 1) show a maximum for PMMA as solvent composition is varied. The maximum in A_2 is at about 0.65 volume fraction of acetonitrile with butanol, 0.60 for propanol, and 0.75 for methanol. It can be seen that,

judging from the second virial coefficient, the methanol mixtures at 25°C are all in the theta-solvent range.

Experimental Procedures

Thin films (about 1 μm thick) of polymer were spun on silicon wafers and baked 1 h at 150°C to remove casting solvent. Two samples of PMMA were used for most of the tests (Table 1). Molecular weights were determined using a Size Exclusion Chromatography system calibrated with PMMA standards. In looking at the effect of water on other systems, several other polymers were used. Solvents were reagent grade and used as received.

A laser interferometer was used for the measurement of dissolution rates[5-8]. The beam from an unpolarized He-Ne laser (2 mW, 632.8 nm) was reflected at an angle of about 10° from the surface of a coated wafer immersed in the liquid mixture. Reflected light intensity was monitored using a photocell and amplifier connected to a strip-chart recorder. The periodicity of the reflected light intensity was used to calculate the rate of dissolution.

Results and Discussion

Figure 2 illustrates the dissolution behavior of the system PMMA, acetonitrile, and 1-butanol at 20°C. The rate plotted represents the actual dissolution rate for the solvent compositions that resulted in smooth dissolution. However, for the compositions noted as only swelling, or partially dissolving, the sinusoidal oscillations in the reflected light intensity are an indication of solvent penetration. There were four regimes of behavior: smooth dissolution of all polymer, dissolution of most of the film but leaving a thin residual film, swelling

with little dissolution, and no observable penetration of solvent.

The region of smooth dissolution extended to 100% acetonitrile only for the low molecular weight PMMA. This is consistent with the findings of Prolongo[3]. At lower concentrations of acetonitrile is a region where residual films were left. The molecular weight of these residues should be higher than the starting material if the solvent is extracting the lower molecular weight portions of the polymer distribution. In one test, a high molecular weight PMMA (KTI Chemicals, Inc.) was exposed to a 50:50 mixture of methanol and acetonitrile. Interferometry confirmed rapid swelling, but only a small amount of dissolution. The final residue had $M_n = 59 \times 10^4$ and $M_w = 115 \times 10^4$ compared to the starting material which had $M_n = 37 \times 10^4$ and $M_w = 106 \times 10^4$. Extraction of about 10% of a low molecular weight fraction from the original film would account for the difference. The final film was rough and the change in thickness could not be estimated accurately. When n-butanol was used alone, there was no visible change observed by interferometry, although a few percent of swelling may have occurred.

The same pattern of behavior was also seen for the PMMA/acetonitrile/methanol system (Figure 3). In comparison with n-butanol, methanol shows more swelling at high alcohol concentrations and a smaller range of smooth dissolution (for the high molecular weight PMMA). Other alcohols were used in an effort to generalize the observed behavior (Table 2, Figure 4). It can be seen that there is a minimum in the dissolution rate at 2-propanol. Within the limits of experimental reproducibility, there appeared to be no difference between 2-propanol and 1-propanol. A "normalized" plot of relative dissolution rate versus size of alcohol does reduce the data for two molecular weights of PMMA

and two alcohol/acetonitrile ratios to a single line (Figure 5). An effort was made to see if the upward trend of rate with alcohol size might continue by using 1-hexanol. Interpretation of residual films and so on was complicated by the low volatility of the higher alcohol. However, at a concentration of 80% acetonitrile, 1-hexanol does appear to dissolve the PMMA (both molelcular weights), but the relative dissolution rate was about equal to that for 1-butanol.

It is striking that the dissolution rate versus solvent composition curves are qualitatively the same for all the alcohols investigated. Regardless of the differences in molecular weight of the PMMA or the absolute values of dissolution rate, the peak rate invariably occurs at an acetonitrile weight fraction of 0.70 ± 0.02. This is in contrast to the behavior of the second virial coefficient (Fig. 1) which peaks about 0.65 for butanol and about 0.75 for methanol. Moreover, the dissolution rate in methanol mixtures is faster than in butanol mixtures (Figures 2 and 3) whereas the thermodynamic criterion A_2 indicates that methanol seldom is much more than a theta solvent.

The smaller range for smooth dissolution with methanol mixtures compared to butanol mixtures is consistent with the A_2 data. There is a smaller thermodynamic "window" giving complete dissolution. On the other hand, the more rapid rate exhibited by methanol illustrates the importance of diffusion on the dissolution process. Diffusivity depends strongly on the molecular size of the diffusing molecule. In the present work, it is apparent that the hydrogen-bonding tendency of the hydroxyl group also enters in.

In another kind of experiment, the addition of a non-solvent to a

solvent has been found to increase dissolution rate. Cooper found that addition of 5% water or 20% methanol to 2-butanone doubled the dissolution rate of PMMA[8]. The same two solvents have an analogous qualitative effect on polystyrene dissolving in 4-methyl-2-pentanone (methyl isobutyl ketone) except that the dissolution rate is affected less and the amounts of non-solvent are lower (Figure 6). The fact that polystyrene does not possess the polar ester groups of PMMA indicates that the increase in dissolution rate is very likely dominated by the faster diffusion of the small molecules rather than polar interactions.

Recently, Katime and co-workers[9] have reported an anomalous effect in the behavior of methanol:4-methyl-2-pentanone mixtures. In the range of 10 to 14 volume % methanol, both the intrinsic viscosity and A_2 change in unexpected fashion. Katime reasons that the hydroxyl group of methanol interacts with the PMMA to give a peak in intrinsic viscosity.

The desirability of a solvent, as described earlier, depends on the criterion chosen. "Goodness" in the thermodynamic sense does not guarantee fast dissolution but it is a necessary property to obtain complete dissolution. In Table 3 are summarized some criteria for judging the suitability for three alcohols mixed with acetonitrile. The equilibirum criterion of high A_2 favors propanol and butanol as "good" solvents. The maximum value of A_2 is obtained with a higher fraction of propanol than butanol, indicating it is the more tolerated additive, ie., the better solvent. The dynamic criterion of dissolution rate ranks the three alcohols in exactly the opposite order. Methanol dissolves fastest, propanol slowest. The volume fraction of alcohol in the mixture

with acetonitrile at the maximum rate of dissolution does not distinguish among the three alcohols.

An explanation often given for the ability of a combination non-solvents to dissolve a polymer involves the solubility parameter concept[11]. In order to generalize the interaction of solvents with polymers, the cohesive energy density holding molecules together in the liquid state (as opposed to the gaseous state) can be subdivided into energies due to dipoles, energy due to hydrogen bonding, and energy due to dispersion forces. The square root of each of these energy densities is a solubility parameter, δ. Typical values for materials used in this study are summarized in Table 4. Using the fractional contribution of each energy term allows presentation of data on a triangular plot (Figure 7). The position of PMMA on the plot is consistent with the fact that three good solvents for PMMA -methyl ethyl ketone (MEK), tetrahydrofuran (THF), and chlorobenzene - are in the same region of the triangular map. However, acetonitrile is far removed from PMMA, and there is no obvious advantage to mixing it with the alcohols. Looking at it another way, a 1:1 mixture of cyclohexane and n-butanol should be a solvent if the solubility concept is valid. The mixture, in fact, does not dissolve PMMA.

The importance of diffusivities in dissolution should be obvious. With the usual assumption of diffusivity varying with the 2/3 power of the molecular volume, it is easy to see why methanol mixtures dissolve PMMA faster than ethanol or propanol mixtures. However, when butanol and hexanol are compared with propanol, perhaps the lower diffusivity of the larger alcohols is compensated for by their solubility parameters being closer to that of the polymer.

Conclusions

Mixtures of acetonitrile with various lower alcohols dissolve high molecular weight PMMA at 20°C even though neither acetonitrile nor the alcohols are solvents when used alone. Rapid diffusion of methanol allows it to form a mixture that dissolves PMMA almost twice as fast as alcohols with 2 to 6 carbon atoms despite the fact that it does not interact thermodynamically as effectively. The second virial coefficient variation with solvent composition indicates that 70 volume % methanol in acetonitrile is a theta solvent for PMMA (A_2 near zero) whereas 70 volume % 1-butanol is a "good" solvent (A_2 over 2×10^{-4} $cm^3g^{-1}mol$). Selection of solvents for dissolution steps in critical operations like microlithography obviously cannot be based purely on thermodynamic measurements.

Acknowledgments

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Table 1   Polymers , poly(methyl methacrylate)

Identification	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	Polydispersity
Low (Elvacite 2008)*	18.6	57.6	3.1
High (Elvacite 2041)*	211	605	2.9

*E. I. duPont de Nemours Corp.

Table 2

Dimensionless Dissolution Rates for mixtures of alcohols with acetonitrile, at 20°C, using the rate with 2-propanol to normalize.

	Low Mol. Wt. PMMA		High Mol. Wt. PMMA		Average
Vol.% alcohol	50	20	50	20	value
Methanol	1.77	1.78	1.54	2.02	1.78
Ethanol	1.34	1.37	1.15	1.38	1.31
1-Propanol	1.02	- - - -	0.97	- - - -	1.0
2-Propanol	1	1	1	1	1
1-Butanol	1.19	1.29	1.06	1.28	1.21
2-Butanol	1.03	- - - -	1.01	- - - -	1.02
1-Hexanol	- - - -	1.18	- - - -	1.21	1.19

Table 3 Comparison of alcohols as co-solvents with acetonitrile for PMMA

| Criterion	Alcohol		
Equilibrium	Methanol	1-Propanol	1-Butanol
Maximum value of A_2, $cm^3g^{-1}mol$	0.4	2.3	2.3
Volume fraction of alcohol at $(A_2)_{max}$	0.25	0.45	0.35
Same at $[\eta]_{max}$	---	---	0.45
Dynamic			
Relative rate of dissolution	2.0	1.0	1.3
Volume fraction of alcohol at $(DR)_{max}$	0.30	0.30	0.30

Table 4　Solubility Parameters[11]

| | Solubility parameter, $(MPa)^{1/2}$ | | | |
| | Non-polar | Polar | H-bond | Total |
	δ_d	δ_p	δ_h	δ_T
Acetonitrile	10.3	11.1	19.6	24.8
Methanol	11.6	13.0	24.0	29.7
Ethanol	12.6	11.2	20.0	26.1
1-Propanol	14.1	10.5	17.7	24.9
2-Propanol	14.0	9.8	16.0	23.4
1-Butanol	15.0	10.0	15.4	28.7
2-Butanol	14.5	9.1	14.8	22.7
1-Hexanol	15.0	8.5	13.7	22.0
Poly(methyl methacrylate)	17.5	5.7	7.8	20.0
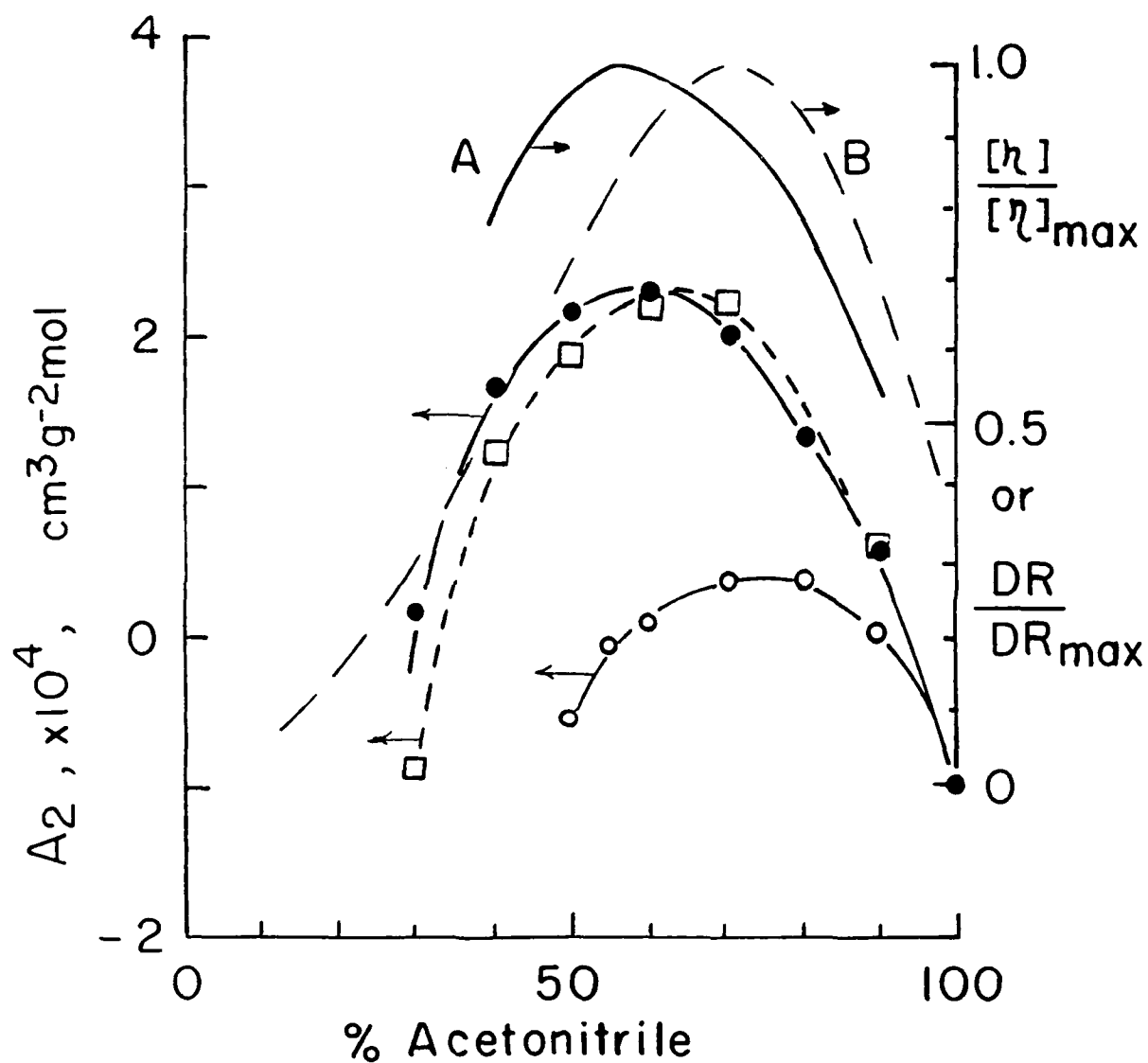
1. Effect of solvent composition on second virial coefficient A_2 (25°C) intrinsic viscosity $[\eta]$ (25°C), and dissolution rate, DR for PMMA (20°C). A., $[\eta]$ in 1-butanol mixtures[3]; B., DR in all alcohols tested (present work); and A_2 in mixtures[3] with C., 1-butanol; D., 1-propanol, and E., methanol.
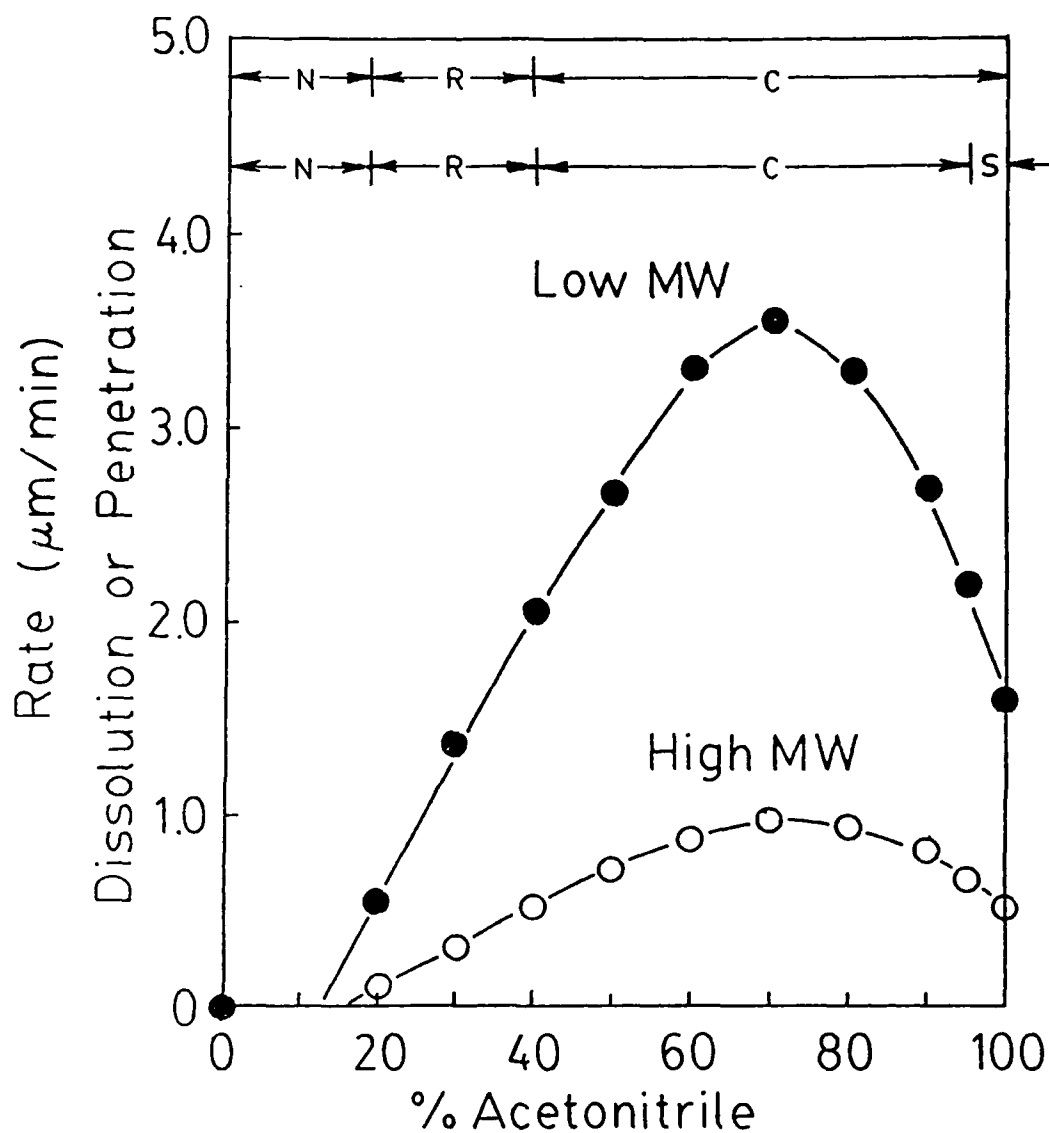
2. Dissolution behavior of PMMA in mixtures of 1-butanol with acetonitrile at 20°C. N = no penetration, S = swelling only, R = dissolution with residue, and C = clean dissolution.
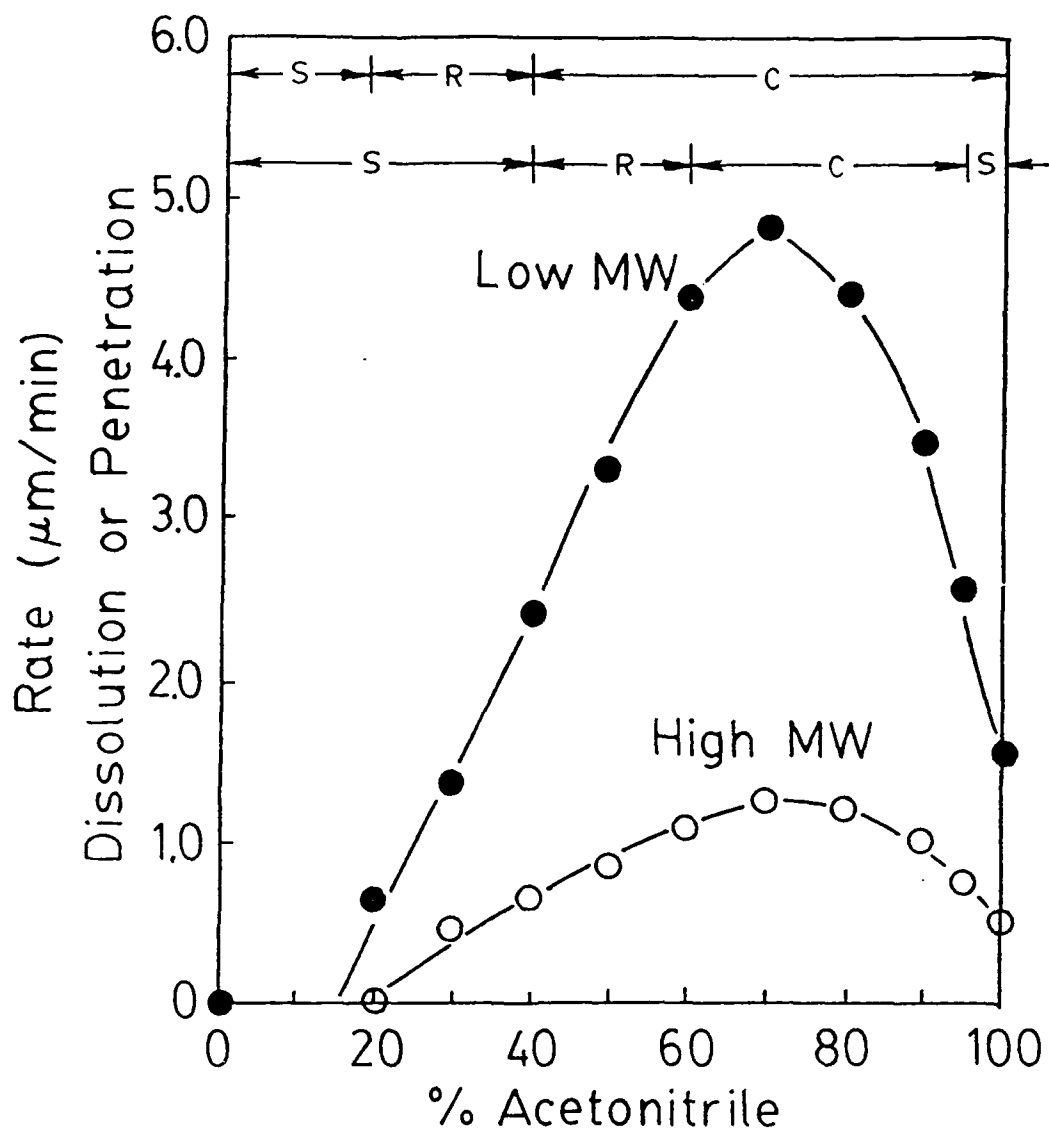
3. Dissolution behavior of PMMA in mixtures of methanol with acetonitrile at 20°C. N = no penetration, S = swelling only, R = dissolution with residue, and C = clean dissolution.
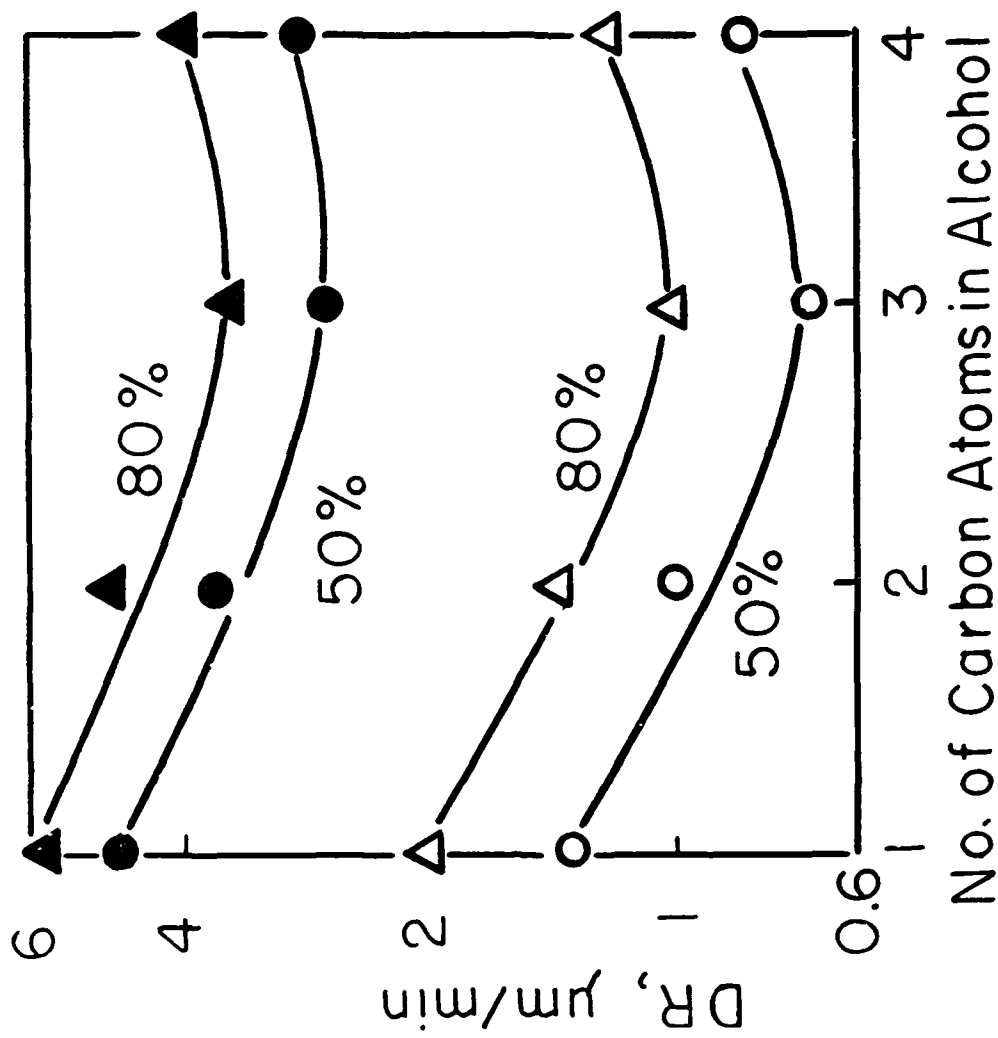
4. Effect of molecular size of alcohol on dissolution rate. Actual rates for high (hollow symbols) and low (solid symbols) molecular weights of PMMA are shown at two concentrations of acetonitrile.
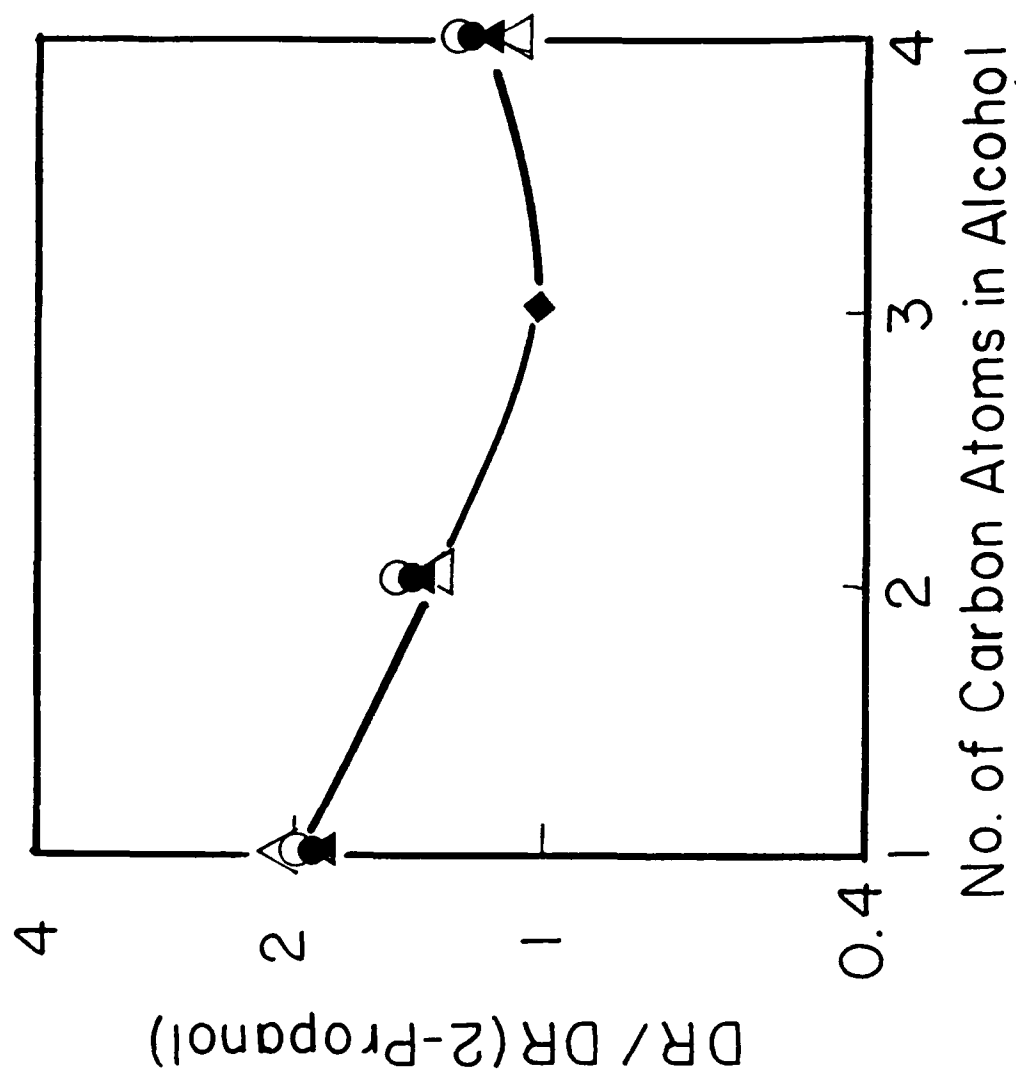
5. Reduced rates for data of Figure 4 normalized by dissolution rate of the 2-propanol mixture with the same concentration of acetonitrile.
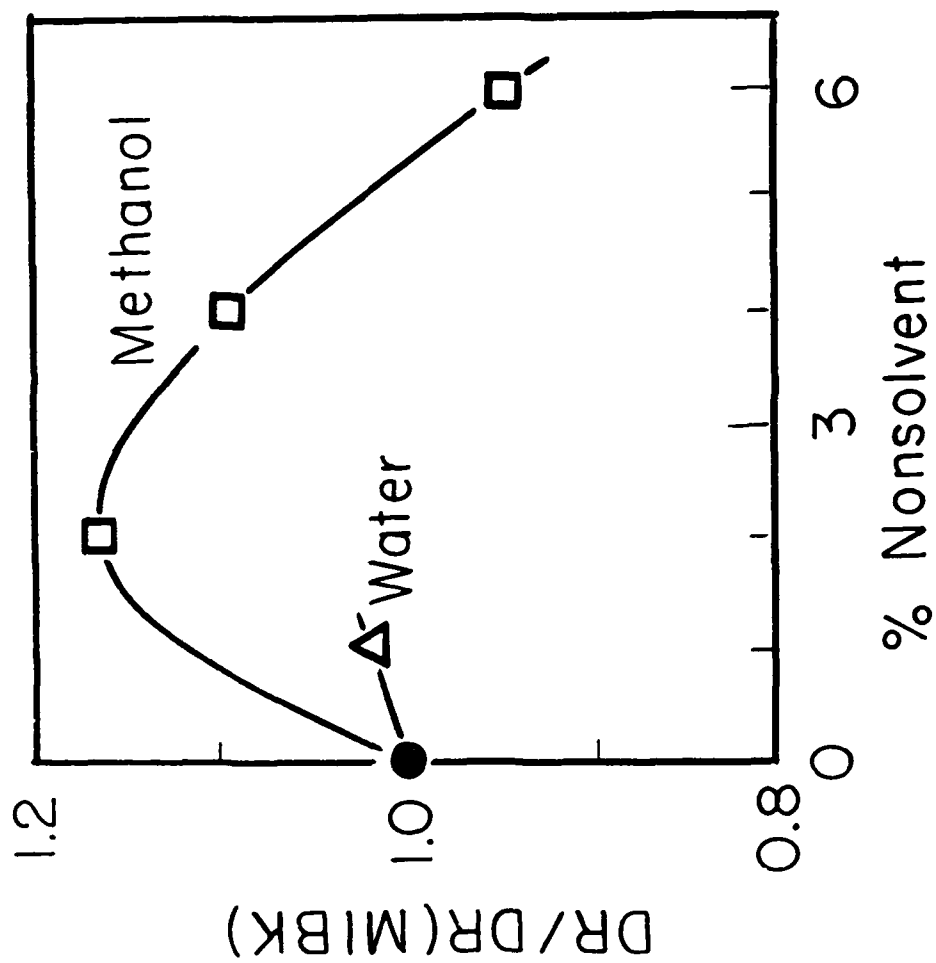
6. Acceleration of dissolution of polystyrene by addition of water or methanol to methyl isobutyl ketone.
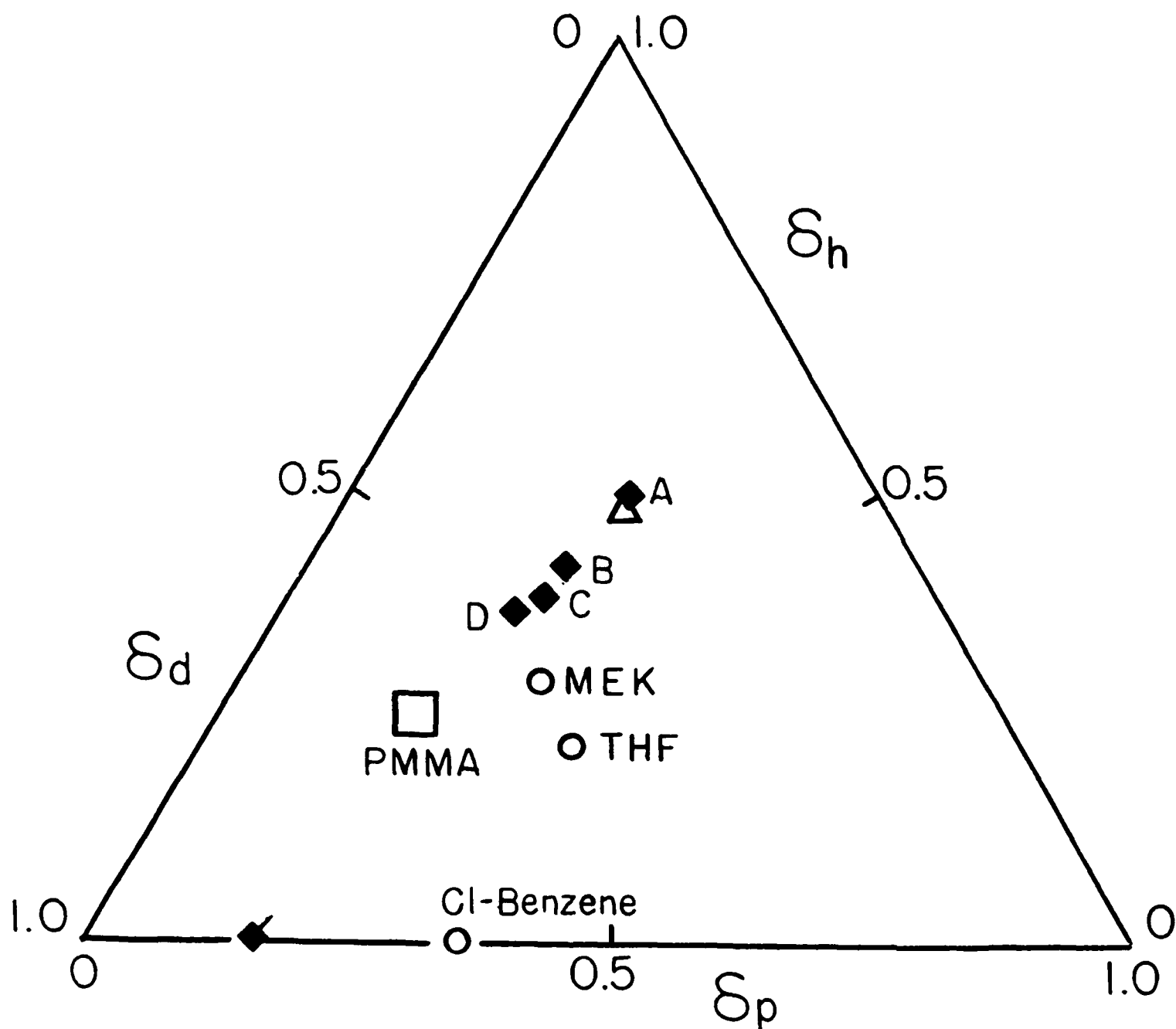
7. Solubility parameter map showing positions of PMMA, 3 solvents (o), acetonitrile ($\triangle$), 4 alcohols ($\blacklozenge$, A = methanol, B = 1-propanol, C = 1-butanol, and D = 1-hexanol), and cyclohexane ($\blacklozenge$).

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